Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 719

Chemical Modification of Lignin-Rich Paper
Part 8: Effect of Light Source on the Accelerated Light-Induced Yellowing of Untreated and Acetylated High-Yield Pulps

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April 1998

Submitted to
Nordic Pulp and Paper Research Journal

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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Chemical modification of lignin-rich paper

Part 8. Effect of light source on the accelerated light-induced yellowing of untreated and acetylated high-yield pulps

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Keywords: Acetylation, Thermomechanical pulp, Chemithermomechanical pulp, Yellowing, Photobleaching, Inhibition, Light source, Hydrogen-peroxide-bleached, Dithionite-bleached, Ultraviolet absorbers

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SUMMARY: The effect of three different irradiation sources (e.g., ultraviolet "blacklight" fluorescent lamps, UV/VIS-fluorescent lamps, and a xenon lamp) on the photoyellowing properties of dithionite-bleached and hydrogen-peroxide-bleached spruce thermomechanical pulp (TMP) and hydrogen-peroxide-bleached spruce and aspen chemithermomechanical pulp (CTMP) has been examined. The aging response of additive-treated (e.g., UV-screen) and/or chemical-modified (acetylated), high-yield pulps toward the tested light sources is also highlighted.

The order of light-induced discoloration, of the different high-yield pulps examined, was determined to be: hydrogen-peroxide-bleached spruce TMP>hydrogen-peroxide-bleached spruce CTMP>dithionite-bleached spruce TMP>>hydrogen-peroxide-bleached aspen CTMP (pretreated with hydrogen peroxide). The spectral distribution of the tested light sources did only marginally alter the aging response of the unmodified, dithionite-bleached, and hydrogen-peroxide-bleached spruce pulps, whereas the high-brightness aspen CTMP showed some variation in the degree of brightness reversion. The acetylated and UV-screen impregnated pulps were, however, strongly dependent on the light source used, which emphasizes the importance of developing a standard method for accelerating testing and measurements of yellowing of lignin-containing materials that could be generally accepted by the research community.

The improved stability toward light, achieved by acetylation of high-yield pulps, is not only a consequence of retarding the color-forming reactions, but also to some degree an effect of promoting photobleaching reactions, both for nonirradiated and preyellowed pulps.

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The use of mechanical and chemimechanical pulps as constituent in higher grades of printing paper is severely restricted by the rapid color reversion (yellowing) that occurs upon exposure to daylight or indoor illumination. This phenomenon has been attributed to a light-induced oxidation of the lignin present in the pulp. Extensive and comprehensive research, performed during the last decade, has given not only new information about the photochemical reactions causing yellowing, but also information on the potential photostabilizing methods, although no single approach so far has become technically or economically feasible to meet all the needs of the paper industry. Heitner and Schmidt (1991) and Leary (1994) have summarized current knowledge in this field in two comprehensive literature reviews (cf. also Heitner 1993).

The photochemical changes that occur during the irradiation of lignin-rich pulps do not only involve discoloration reactions. Several researchers have reported a photobleaching effect when pulps were irradiated at longer wavelengths. If the color-forming reactions could be eliminated or slowed down, the bleaching reactions would be predominant and result in a brightness increase for high-yield pulps when irradiated in daylight. However, the darkening reactions normally dominate over the brightening reactions, and the net result is a discoloration of the lignin-rich material. The photoyellowing-photobleaching phenomenon has been observed in several investigations. Nolan et al. (1945) reported that the transition between photoyellowing and photobleaching, during irradiation of groundwood pulp (GWP), occurred at 385 nm. UV radiation of wavelengths 290 to 390 nm discolored unbleached and bleached spruce GWP, whereas light in the 420-470 nm range had a photobleaching effect (Andtbacka et al. 1989). It was further noted that the discoloration of the irradiated samples continued during storage in the dark. The most severe brightness loss was shown by the samples irradiated at lower wavelengths. Forsskåhl and Janson (1991) reported that unbleached and bleached chemimechanical pulp responded similarly toward irradiation at selected wavelengths between 280 and 600 nm. The strongest discoloration was observed on irradiation at 310-320 nm (cf. Forsskåhl, Tylli 1993). Forsskåhl and Tylli (1993) reported that the degrees of both photoyellowing and photobleaching were linearly dependent on light intensity. Andrady et al. (1991) used monochromatic radiation in the range of 260-600 nm and found that TMP-based newsprint was discolored on irradiation at short wavelengths in this interval. The transition from yellowing to bleaching was observed between 340 and 400 nm. In a continuation of this work, Andrady and Searle (1995) found that newsprint exposed to polychromatic radiation (similar to terrestrial sunlight) showed the largest amount of yellowing when subjected to irradiation in the wavelength region of 330-385 nm (UV-A region). This means that the wavelengths transmitted through window glass can still cause considerable amounts of yellowing in high-yield paper.

The intensity of sunlight varies with wavelength and passes through a maximum at approximately 470 nm. Most of the ultraviolet component of sunlight that reaches the earth's surface has wavelengths between 293 and 400 nm (Hirt et al. 1960). The total energy below 300 nm is very small, whereas the radiation energy between 300 and 350 nm is approximately one-third of that between 350 and 400 nm. Furthermore, the proportion below 350 nm is reduced indoors because of absorption by window glass. Lignin is a very efficient absorber of both UV radiation (due to its aromatic nature) and visible light, in contrast to cellulose, hemicelluloses, and extractives that have only some absorption in this region (λ>300 nm). This means that most of the absorption in lignocellulosic materials takes place in the lignin constituent. The important region of the sunlight spectrum is that between 300 and 550 nm, because the intensity of the sunlight below 300 nm is low, and the photoactive functional groups in lignin have their absorption maxima in this region (cf. Gratzl 1985).

No standard procedure has been established for the study of the light-induced yellowing of lignocellulosic materials. This complicates the interpretation of the results reported by different researchers. Differences in exposure conditions (humidity, temperature, etc.), light source (light intensity, spectral distribution, etc.), exposure time, grammage of the exposed sample, and the procedure chosen to measure and report the color reversion quantitatively greatly influence the experiments. The development of an accelerated reproducible testing method that could be generally accepted is therefore of considerable importance. (Although accelerated tests give rapid and reproducible testing conditions, subtle effects may be lost due to the high light intensity used.)

When lignocellulosic materials are exposed to light, the brightness reversion is primarily dependent on the wavelength and intensity distribution of the light source used, and it is therefore important to find a light source that simulates the solar spectrum or office illumination as close as possible. Several types of light sources have been used in accelerated tests, including xenon lamps, medium-pressure mercury lamps ("blacklights"), carbon-arc lamps, and sun lamps. Of these, the xenon lamp (used with borosilicate filters to eliminate light below 300 nm) provides a close match to the spectral energy distribution of natural daylight (cf. Hirt et al. 1960; Johnson 1989; Bailey, Lamont 1993).

The present paper describes the effect of irradiation sources with different wavelength distributions on the accelerated light-induced yellowing of untreated and acetylated and/or UV-screen-impregnated high-yield pulps. The effect of sequential irradiation of high-brightness aspen CTMP with different light sources is also discussed.

Experimental

Pulps and paper samples. Commercially produced dithionite-bleached TMP and hydrogen-peroxide-bleached spruce (*Picea abies*) TMP together with hydrogen-peroxide-bleached spruce (*Picea abies*) and aspen (*Populus tremuloides*) CTMP were used as received for the studies described in this paper. The pulps were obtained as dried samples. The high-brightness hardwood CTMP was manufactured employing hydrogen peroxide both as a chemical pretreatment and as a bleaching stage. Handsheets (60 $g \cdot m^{-2}$) were prepared according to TAPPI Test Method T 205 om-88. The paper sheets were then conditioned at 23°C and 50% r.h. according to TAPPI Test Method T 402 om-88 before further treatment.

Solvents and photostabilizing additives. The solvents and the ultraviolet-absorbing additives [2-hydroxy-4-methoxybenzophenone (HMB) and Tinuvin 384 (3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid, C7-9-branched alkyl esters, a benzotriazole derivative supplied by Ciba-Geigy Corporation)] were commercial products and were used as received.

Acetylation procedure. The handsheets [cut into strips (30 x 75 mm)] were acetylated (at 100°C or 110°C) according to the procedure described by Paulsson et al. (1994).

Impregnation procedure. Weighted amounts of ultraviolet-absorbing additives were dissolved in methanol (HMB) or acetone (Tinuvin 384) and sprayed onto handsheets. All experiments were replicated a minimum of two times.

Analyses. The acetyl content was calculated from the amount of acetate liberated after saponification with sodium hydroxide as previously described in Paulsson et al. (1996a). The acetyl content is given as a percentage of the dry weight of the paper. The amount of photostabilizing additive applied onto the handsheets was determined by weighing the handsheets prior to addition

and after reequilibrating of the treated handsheets (at 23°C and 50% r.h.). The addition level is given as a percentage of the conditioned weight of the paper.

Accelerated light-induced yellowing. The paper samples were subjected to an accelerated photoyellowing in a Rayonet photochemical reactor (Model RPR 100, The Southern New England Ultraviolet Company, Branford, CT, USA) equipped with eight RPR 3500Å UV-fluorescent lamps ("blacklight," The Southern New England Ultraviolet Company) or eight RPR 5750Å UV/VIS-fluorescent lamps (The Southern New England Ultraviolet Company) and a merry-go-round apparatus for uniform irradiation. The temperature was kept close to room temperature by a cooling fan (to minimize heating of the sample). Accelerating reversion studies were also conducted with a SUNTEST CPS (Heraeus HANAU, Hanau, Ger.) light-aging tester equipped with a xenon burner and filters (ultraviolet and window-glass), which eliminate radiation of wavelengths below 310 nm. The spectral distribution of the transmitted light was similar to that of average indoor daylight. The temperature was kept close to room temperature by a cooling fan. The irradiance was controlled by an optical sensor that compensates for possible main voltage fluctuations and burner aging. Untreated paper sheets were used in all radiation experiments as controls.

Optical measurements. TAPPI brightness and color changes according to the CIELAB color scale (L^*-, a^*-, b^*-values) were measured using a Technidyne Brightimeter (Model S-5) according to TAPPI Test Method T 452 om-92 and TAPPI Test Method T 524 om-94, respectively. The reflectance of a single sheet of paper (60 $g \cdot m^{-2}$) over a completely black, nonreflecting surface (over a hollow black body, reflectance <0.5%) and the reflectance over a stack of paper (high enough to inhibit any transparence of light) were recorded. The specific light scattering coefficient (s, at 457 nm) was then calculated using the Kubelka-Munk theory. Optical properties of the SUNTEST CPS irradiated handsheets were measured using an Elrepho 2000 spectrophotometer. The post color (PC) number (at 457 nm, according to Giertz 1945) was calculated for the treatment with ultraviolet absorbing additive and/or acetylation (PC_1) and for the light-induced reversion (PC_2) (cf. Janson, Forsskåhl 1989). The sum of PC_1 and PC_2 represents the total effect of the treatment: $PC = PC_1 + PC_2$. The change in specific light-absorption coefficient (Δk, at 457 nm) during irradiation was calculated from the PC_2-value with the assumption of constant light scattering according to Johnson (1989).

Results and discussion

Light sources and measurements of the rate of yellowing

To assess the importance of the wavelength distribution of irradiation sources used for accelerated reversion tests, a series of handsheets made from untreated and acetylated high-yield pulps were irradiated with three different light sources, and the optical properties were monitored. The light sources chosen were ultraviolet fluorescent lamps ("blacklight," RPR 3500Å), UV/VIS-fluorescent lamps (RPR 5750Å), and a xenon burner, i.e., commonly used irradiation sources in many light-induced aging equipments. The UV-fluorescent lamps emit light in a band between 300 and 420 nm (approximate Gaussian spectral distribution, λ_{max} = 350 nm), i.e., the visible component of diffuse sunlight or office light is practically missing. The UV-fluorescent lamps give an assessment of the UV light-aging properties and could be useful when complications from other wavelengths are not desirable. The UV/VIS-fluorescent lamps emit light in the ultraviolet and visible range (from about 350 to 700 nm, λ_{max} = 575 nm) and have a comparatively close match to the conventional standard "cool white" fluorescent color used in many commercial lighting

installations. The energy distribution is enriched at 575 nm, i.e., most of the light is emitted in the visible part of the spectrum. The spectral distribution of the transmitted light from the xenon lamp (nominal rating of xenon burner, 1.1 kW) and filter combinations used was similar to that of average indoor daylight. The temperatures during irradiation were 29°C, 27°C, and 30°C for the UV-fluorescent lamps, UV/VIS-fluorescent lamps, and xenon lamp, respectively. Figures 1a-c summarize the spectral distribution of the three light sources, as received from the manufacturers. The spectral distribution of standard "cool white" fluorescent color (Waymouth 1992) and natural daylight (Merrigan 1975) is given, as a comparison, in Figs. 1b (broken line) and 1c (dotted line), respectively. The use of controls in each irradiation experiment and the exchange of UV/VIS-fluorescent lamps between aging series were done to monitor and minimize the effects of aging of the light sources studied.

The yellow color generated during the irradiation of high-yield pulps is caused by the formation of chromophores absorbing in the blue region of the spectrum. The changes in optical properties that occur can be characterized in several ways. One possibility is to express the degree of yellowing as the post color (PC) number (often given at 457 nm). The Kubelka-Munk equation is used to calculate $k \cdot s^{-1}$ according to Eq. [1] (Giertz 1945). In this formula, R_∞ is the reflectance of an optically thick (opaque) sheet. The PC-number is then calculated according to Eq. [2] where t is the irradiation time, k the specific light absorption coefficient, and s the specific light scattering coefficient.

$$k \cdot s^{-1} = [(1-R_\infty)^2 \cdot (2 \cdot R_\infty)^{-1}] \qquad [1]$$

$$\text{PC-number} = 100 \cdot [(k \cdot s^{-1})_t - (k \cdot s^{-1})_{t=0}] \qquad [2]$$

$$\Delta k = s_0 \cdot \text{PC-number}/100 \qquad [3]$$

Because the light-induced photodegradation is most pronounced at the surface, the distribution of chromophores formed is not homogenous throughout the paper cross section (cf. Eriksson et al. 1988; Johnson 1989; Luo, Göttsching 1991; Forsskåhl et al. 1995a, b). The use of the Kubelka-Munk function is restricted because it is based on the assumption that the sample is homogenous. Furthermore, the post color number cannot compensate for large differences in light scattering when two samples with different s-values are compared. The inhomogeneity in chromophore distribution in the irradiated paper samples can be overcome by using thin sheets (grammage of approximately 10 $g \cdot m^{-2}$) because they are illuminated almost evenly throughout their thicknesses (Heitner, Min 1987; Schmidt, Heitner 1993). Because the formation, i.e., homogeneity regarding fibers, fines, fillers, etc., required by the Kubelka-Munk theory could not be fulfilled with such a low grammage, a grammage of 30-40 $g \cdot m^{-2}$ for high-yield pulps is recommended to minimize the errors caused by nonuniform formation (Lejong et al. 1987). The light absorption coefficient (k) of a sheet of paper is a parameter that is linear with respect to the chromophore content of the pulp, i.e., the brightness reversion can be expressed as the change in the light absorption coefficient. The inhomogeneity of the irradiated sample is, however, still a problem. A closer description of the change in color can be obtained from the L^*-, a^*-, and b^*-values according to the CIELAB color system. Measurement of the brightness loss is a convenient and fast method, but it can only be used to compare samples with the same initial brightness (a consequence of the Kubelka-Munk

relationship). The brightness is, however, of the utmost importance, because the PC-number gives information only about the changes that occur during irradiation (modification, etc.) and not about the absolute values reached after treatment. Furthermore, the brightness concept is in general use, i.e., both the researcher and the paper manufacturer can evaluate the effects of a light-stabilizing treatment.

In this work, the optical properties were measured on 60 $g \cdot m^{-2}$ paper sheets. The PC-number was then calculated according to equations [1] and [2] and the change in light absorption coefficient (Δk) according to equation [3] (based on the assumption of constant light scattering, s_0) according to Johnson (1989). Although the post color number is not an exact tool for kinetic studies, it gives an adequate approximation of the degree of yellowing under the different aging conditions studied. Furthermore, color measurements (i.e., L^*-, a^*-, and b^*-values) were monitored in some cases.

Optical properties of irradiated, unacetylated high-yield pulps

Table 1 summarizes the optical properties of unirradiated, unacetylated, and acetylated high-yield pulps. The initial TAPPI brightnesses of the examined pulps were in the range between 65.7 and 84.3%, i.e., representing pulps with a wide range of initial chromophore contents.

Figures 2a-c and Table 2 show the effect of different light sources on the photoyellowing of the pulps. The dithionite-bleached spruce TMP was used as a control to determine the different periods of irradiation that were needed to obtain an approximately equivalent degree of light-induced reversion under the test conditions used. The comparison was made at 4, 216 (9 days), and 40 hours for the UV-fluorescent lamps, UV/VIS-fluorescent lamps, and xenon burner aged sheets, respectively. As can be seen in Figs. 2a and c, the yellowing of the UV-fluorescent lamps and xenon lamp irradiated sheets is characterized by a rapid initial phase that is followed by a slower phase. This is the general behavior of the discoloration process that has been reported by several researchers (Lewis et al. 1945; Francis et al. 1991; Ek 1992; Paulsson et al. 1996a). When the UV/VIS-fluorescent lamps were used as an irradiation source, the initial rapid phase was less pronounced, resulting in flatter brightness curves, especially for the high-brightness aspen CTMP (Fig. 2b). It is also evident that the degree of yellowing was somewhat more pronounced (larger Δk) for the hydrogen-peroxide-bleached spruce TMP and CTMP than for the dithionite-bleached spruce TMP (cf. Gellerstedt et al. 1983; Francis et al. 1991; Paulsson et al. 1996a). The Δk-values obtained were in the ranges 10-11 and 11-13 for the dithionite-bleached and hydrogen-peroxide-bleached pulps, respectively (Table 2). Furthermore, the bleached spruce CTMP was somewhat more stable than the bleached spruce TMP, as reported previously (Heitner, Min 1987; Johnson 1989; Schmidt, Heitner 1995). For practical purposes, however, the decrease in brightness is sufficient to cause a visible discoloration in a short period of time that limits the field of application for all of the softwood pulps tested.

Hardwood pulps have been reported to be more resistant toward light-induced aging than softwood pulps (Janson, Forsskåhl 1989; Johnson 1989; cf. Forsskåhl, Janson 1992). The rate of light-induced chromophore formation was significantly lower for the aspen CTMP compared with the other pulps examined in this investigation, and the variation in obtained aging results, between the different exposure techniques used, was larger. The change in light absorption coefficient (Δk) was between 2.7 and 6.2, i.e., ca. 40 to 75% lower than that for the softwood pulps (cf. Table 2).

In conclusion, with the exception of the high-brightness aspen CTMP, the different irradiation sources gave comparable aging results for all of the unmodified, bleached softwood pulps tested.

The spectral distribution of the light sources did only marginally alter the photoyellowing characteristics of the examined softwood pulps.

Optical properties of irradiated, acetylated high-yield pulps

To establish if chemical modification (e.g., acetylation) of the pulps altered the aging response toward the tested irradiation sources, a series of test sheets were acetylated to various degrees. As can be seen in Table 1, the acetylation treatment resulted in a small brightness gain for the dithionite-bleached TMP (about 2 brightness units) and a small brightness loss for the hydrogen-peroxide-bleached spruce pulps (about 2.5 brightness units). The brightness loss for the hydrogen-peroxide-pretreated high-brightness aspen CTMP was more severe; an acetylation time of 25 minutes resulted in a brightness loss of more than 10 brightness units. The change in optical properties was manifested as an increase in the lightness (L^*) and a decrease in the yellowness (b^*) for the dithionite-bleached TMP, whereas the opposite was true for the hydrogen-peroxide-bleached pulps. In all cases, the change in a^*-value (green-red color vector in the three-dimensional color scale) was small. These findings agree well with results from earlier investigations (Paulsson et al. 1994; Paulsson, Ragauskas 1997).

As can be seen in Figs. 3 to 6 and Table 2, acetylation strongly inhibited the photoyellowing as previously reported (Paulsson et al. 1995; Paulsson et al. 1996a). Figure 3 illustrates the effect of light source on the yellowing properties of acetylated, dithionite-bleached TMP sheets. When irradiated with the UV/VIS-fluorescent lamps or xenon lamp, a photobleaching of the acetylated sheets took place. The effect was more pronounced for the UV/VIS-fluorescent lamps than for the xenon lamp (only a small initial brightness increase). As expected, the most severe yellowing (no photobleaching) was observed when the TMP sheets were irradiated with the UV-lamps (emit almost no light in the visible range). The PC_2-values after irradiation were -0.5 (UV/VIS-fluorescent lamps, i.e., negative sign indicates that the paper still is brighter than before irradiation), 5.5 (xenon lamp), and 9.3 (UV-fluorescent lamps) for the high acetylated TMP, see Table 2. This corresponds to a difference in brightness of more than 12 units after irradiation.

The change in brightness for the two acetylated hydrogen-peroxide-bleached spruce pulps is shown in Fig. 4 (TMP) and Fig. 5 (CTMP). Generally, the effect of the different irradiation sources was the same as for the unbleached TMP, although the photobleaching effect was smaller and obtained only for the pulps irradiated with the UV/VIS-fluorescent lamps. The difference in reverted brightness was about 11 brightness units for the low acetylated pulps (acetyl content of 3.5 to 4.6%) and more than 14 units for the high acetylated pulps (acetyl content, 6.7-9.4%) (Table 2).

The degree of reversion caused by the different light sources was in the order UV->xenon>> UV/VIS-lamps for the acetylated aspen CTMP (Fig. 6), i.e., the same order as for the other acetylated pulps. The UV/VIS-fluorescent lamps induced a rapid and strong photobleaching of the acetylated samples. The TAPPI brightness was ca. 82% after 24 hours of irradiation for all of the acetylated samples, which corresponds to a brightness gain of 1 to 8 brightness units depending on the derivatization degree studied. Thus, most of the colored substances formed on acetylation of hydrogen-peroxide-pretreated aspen CTMP can easily be converted to colorless structures during irradiation with visible light.

The photobleaching (a decrease in light absorption at $\lambda_{max} \approx 360$ nm) observed on irradiation of milled wood lignin (MWL) and high-yield pulps has been attributed to the photooxidation of coniferaldehyde end groups in lignin to produce vanillin-type end groups (Wang et al. 1993; Wang et al. 1995). Furthermore, the dissimilarities in the absorption difference spectra of peroxide-

bleached softwood TMP and peroxide-bleached softwood CTMP have been explained in terms of coniferaldehyde photobleaching (Schmidt, Heitner 1995). It is also possible that quinonoid structures, absorbing in the blue-green region of the spectrum, photochemically convert to colorless structures (for general comments on light-induced reactions of quinones, cf. Bruce 1967; Bruce 1974). This has been demonstrated in the case of methoxy-*p*-benzoquinone incorporated in a solid carbohydrate matrix (i.e., 2-hydroxypropylcellulose); the photoreduction to methoxy-hydroquinone was a rapid process, whereas the photooxidation of the hydroquinone was comparatively slow (Castellan et al. 1993). Ragauskas (1993) reported that simple *para-* and *ortho*-quinones, impregnated onto cellulose sheets, did not in general cause any further darkening during irradiation (photolyzed with a xenon lamp). Several of the examined quinones exhibited instead a small brightness increase in the irradiated sheets, which could possibly be attributed to a photobleaching effect. Furthermore, Schmidt et al. (1995) found that methoxylated *ortho*-quinones, introduced into thermomechanical pulp by treatment with Fremy's salt, were bleached by 420 nm irradiation, whereas unmethoxylated *ortho*-quinones, generated by treatment with sodium periodate, were not.

Several researchers have reported that methylated and particularly acetylated lignocellulosic materials can be photobleached during irradiation (Callow 1947; Callow, Speakman 1949; Manchester et al. 1960; Andrews, Des Rosiers 1966; Lorås 1968; Ek et al. 1992; Paulsson et al. 1995). The photobleaching of acetylated materials has been ascribed to the formation of acetyl peroxide or peroxides formed from the carbohydrate acetates during irradiation (Callow, Speakman 1949; Lorås 1968). When comparing the degree of yellowing of acetylated high-yield pulps, aged under different light sources, with the degree of yellowing for untreated high-yield pulps, it is evident that the photostabilization obtained by the acetylation treatment not only is an effect of retarding the color-forming reactions, but also is a result of promoting photobleaching reactions. The results from aging experiments with the UV-fluorescent lamps give an assessment of the UV-light aging properties, i.e., a measurement of the chromophore-retarding effect of acetylation (cf. a in Figs. 3 to 6). The photobleaching response of acetylated pulps is illustrated for the sheets aged with the UV/VIS-fluorescent lamps (b in Figs. 3 to 6).

It is difficult to explain the photobleaching effect, obtained for acetylated mechanical pulps, in terms of coniferaldehyde or *ortho*-quinone photobleaching. The brightening effect of hydrogen peroxide has been attributed to a reaction with chromophoric carbonyl structures in the lignin. Several investigations have shown that hydrogen peroxide bleaching removes most (but not all) of the coniferaldehyde units in the lignin (Hirashima, Sumimoto 1987; Pan et al. 1992; Pan et al. 1994; Agarwal, McSweeny 1995; Agarwal et al. 1995; Schmidt, Heitner 1995). Quinone- and coniferaldehyde-type chromophores can also be eliminated by reaction with dithionite (cf. Dence, Reeve 1996). Furthermore, model compound studies have shown that acetylation rapidly decomposes most of the *ortho*-quinone units, whereas the *para*-quinones were essentially unaffected (Paulsson et al. 1996b). The significance of the remaining coniferaldehyde structures, *ortho-* and *para*-quinones, diguaiacylstilbenes (cf. Castellan et al. 1990; Gellerstedt, Zhang 1992; Gellerstedt, Zhang 1993; the term guaiacyl refers to a 4-hydroxy-3-methoxyphenyl residue), or some other still unknown structure for the photobleaching (and brightness stability) needs to be investigated further.

Optical properties of irradiated, acetylated and/or UV-screen impregnated aspen CTMP

A previous investigation has shown that efficient inhibition of photoyellowing was obtained when moderate amounts of UV-screens, such as 2-hydroxy-4-methoxybenzophenone (HMB) or Tinuvin

384 (a benzotriazole derivative), were applied onto acetylated sheets (Paulsson, Ragauskas 1997). Fig. 7 and Table 3 shows the change in optical properties during irradiation of acetylated and/or HMB-treated sheets made of hydrogen-peroxide-bleached aspen CTMP. The effect of Tinuvin 384 was, in general, the same, and will therefore not be discussed further. As can be seen in the figure, the irradiation source chosen for reversion studies of additive-treated (or chemically modified) high-yield pulps has a crucial role in the outcome of the experiments and thereby the judgment of the effectiveness of a photostabilizing treatment. The HMB-treated sheets exhibited a good photostability when exposed to UV-radiation, probably due to a good match of the wavelength distribution of the light source (see Fig. 7a). When exposed to a broader wavelength range, the photostabilizing effect of the UV- absorbing compounds was different. Although UV/VIS-fluorescent lamps emit light in the ultraviolet range, the HMB-treated sheets showed no increased resistance toward photoaging when irradiated with this light source as compared to the control or acetylated sheets, respectively (Fig. 7b). The use of the xenon light source (Fig. 7c) gave aging results that were comparable with those obtained with the UV-lamps, although the photostabilizing effect of UV-screens were less and the effect of acetylation more pronounced than was the case when subjected to ultraviolet radiation alone.

Although the different light sources tested in this investigation gave a comparable degree of reversion for most of the untreated pulps, the effect of different irradiation techniques, i.e., spectral distribution of the light source used, considerably altered the photostabilizing effect of chemical modification (e.g., acetylation) and addition of UV-screens. The discrepancy in effectiveness of an inhibiting treatment reported in the literature can, in many cases, be explained in terms of the different exposure techniques used by the researcher/laboratory.

Sequential irradiation of untreated and acetylated, high-brightness aspen CTMP using UV- and UV/VIS-fluorescent lamps

The changes in TAPPI brightness, as a function of irradiation time under different irradiation sources, for the untreated and acetylated hydrogen-peroxide-bleached aspen CTMP are presented in Figures 8a and b. The changes in brightness for the handsheets irradiated with only one light source are given as a comparison in the figure (filled symbols). When comparing the sequence UV-fluorescent lamps – UV/VIS-fluorescent lamps, it is evident that irradiation with wavelengths of 300 to 420 nm generated colored structures that partly could be removed by irradiation with a more broader wavelength range (e.g., visible light). The photobleaching effects for the acetylated, UV-irradiated handsheets were much larger than for the irradiated control; a brightness gain of about 12 brightness units was obtained for the acetylated sheets compared with 7 units for the control (see Fig. 8a). Furthermore, the difference in brightness between the sequential irradiated (UV + UV/VIS) and the UV/VIS irradiated, acetylated CTMP was in the range of 3-4 brightness units after 400 hours of irradiation, i.e., only a small amount of the chromophores generated during UV-exposure of acetylated high-brightness aspen CTMP was not photobleachable. The corresponding value for the control was 7 brightness units. Figure 8b shows the photoyellowing effect of the irradiation sequence UV/VIS-fluorescent lamps – UV-fluorescent lamps. When the CTMP was acetylated to a high degree (acetyl content, 10.3%), the brightness, after the sequential irradiation procedure (400 + 4 h), was almost the same as after UV-exposure alone. There was, however, a decrease in brightness for the low acetylated CTMP (acetyl content of 4.1%, ca. 8.5 brightness units) and for the control (ca. 16.3 units).

The photobleaching of a photoyellowed pulp has been reported by several researchers. Claesson et al. (1968) reports that high-yield bisulfite liner and newsprint made from mechanical pulp discolors on irradiation with ultraviolet radiation of 365 nm, but that a bleaching of the yellow color was observed in visible light (436 nm). Forsskåhl and Tylli (1993) found that the maximum photobleaching of photoyellowed, unbleached, and bleached chemimechanical pulp occurs on irradiation at 420 to 430 nm; the brightening effect was, however, small compared to the discoloration observed. The results from the present investigation have shown that photobleaching of preyellowed (UV-irradiated, λ_{max} = 350 nm), untreated, and acetylated high-brightness aspen CTMP sheets occurs when the sheets are exposed to visible light (e.g., UV/VIS-fluorescent lamps, λ_{max} = 575 nm). It is also evident that acetylation (of the pulp) suppresses the color-forming reactions, while the photobleaching reactions are favored, both for nonirradiated and preyellowed handsheets.

Conclusions

The different irradiation sources used (e.g., ultraviolet "blacklight" fluorescent lamps, UV/VIS-fluorescent lamps, and a xenon burner) gave comparable aging results for the untreated spruce pulps, whereas the high-brightness aspen CTMP showed some variation in the degree of yellowing. The high-brightness aspen CTMP was, however, the most resistant pulp toward irradiation followed by the dithionite-bleached spruce TMP and the hydrogen-peroxide-bleached spruce CTMP. The hydrogen-peroxide-bleached spruce TMP was the most light-sensitive pulp to all of the light sources examined.

The loss in brightness for the acetylated pulps was strongly dependent on the light source used and was in the order: UV-fluorescent lamps>xenon lamp>>UV/VIS-fluorescent lamps. Photobleaching of the acetylated pulps was observed when exposed to radiation from the UV/VIS-fluorescent lamps. Furthermore, the UV-screen treated, high-brightness aspen CTMP showed a good photostabilization effect when exposed to radiation from the UV-fluorescent lamps or xenon lamp, but no retarding effect was observed under aging with the UV/VIS-fluorescent lamps, i.e., the irradiation source used for accelerated aging of chemically modified or additive-impregnated high-yield pulps has a decisive role in the judgment of a photostabilizing treatment.

The chromophores generated during irradiation of aspen CTMP with ultraviolet radiation was found to be partially decolored by exposure to light from the UV/VIS-fluorescent lamps (e.g., visible light, λ_{max} = 575 nm); an effect that was more pronounced for the acetylated pulps. Furthermore, the photostabilizing effect of acetylation is, most likely, a function of both retarding the reactions that generate colored chromophores and promoting photobleaching reactions. These results suggest that, although the acetylation methodology employed to generate UV/VIS-photostable lignin-containing paper not yet are suitable for commercial applications, the photostability of these handsheets is significant. Further studies are needed to determine the fundamental principles contributing to the photobleaching effect of acetylated high-yield pulps.

The present investigation has shown the necessity to develop a standard procedure for accelerated testing of the light-induced aging of lignin-containing materials.

Acknowledgments

Financial support for this work was provided by the Member Companies of the Institute of Paper Science and Technology, USDA Improved Utilization of Wood and Wood Fiber (Contract No. 96-35103-3800) and The Gunnar and Lillian Nicholson Graduate Fellowship and Faculty Exchange Fund. The authors would like to thank Ms. Lena Fogelquist, Department of Forest Products and Chemical Engineering, Chalmers University of Technology, for skilful assistance in the experimental work.

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Figure captions

Fig. 1. Spectral characteristics of the tested irradiation sources. The spectral energy distributions of standard "cool white" fluorescent color (Waymouth 1992) and natural daylight (Merrigan 1975) are given in ***b*** *(broken line) and* ***c*** *(dotted line), respectively. Abbreviations: RPR 3500Å = UV-fluorescent lamps; RPR 5750Å = UV/VIS-fluorescent lamps; Xe = xenon lamp.*

Fig. 2. The change in TAPPI brightness after accelerated light-induced aging of different types of mechanical pulps. Abbreviations as in Fig. 1. Legends: (□), dithionite-bleached spruce TMP; (◊), hydrogen-peroxide-bleached spruce TMP; (○), hydrogen-peroxide-bleached spruce CTMP; (Δ), hydrogen-peroxide-bleached aspen CTMP.

Fig. 3. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and acetylated dithionite-bleached spruce TMP. Abbreviations as in Fig. 1. Legends (acetyl content): (◊), 6.2%; (○), 10.6%.

Fig. 4. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and acetylated hydrogen-peroxide-bleached spruce TMP. Abbreviations as in Fig. 1. Legends (acetyl content): (◊), 3.5%; (○), 6.7%.

Fig. 5. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and acetylated hydrogen-peroxide-bleached spruce CTMP. Abbreviations as in Fig. 1. Legends (acetyl content): (◊), 4.6%; (○), 9.4%.

Fig. 6. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and acetylated hydrogen-peroxide-bleached aspen CTMP. Abbreviations as in Fig. 1. Legends (acetyl content): (◊), 4.1%; (○), 6.0%; (Δ), 9.7%; (∇), 10.3%.

Fig. 7. The change in TAPPI brightness after accelerated light-induced aging of untreated (□), 2-hydroxy-4-methoxybenzophenone-impregnated and/or acetylated hydrogen-peroxide-bleached aspen CTMP. Abbreviations as in Fig. 1. Legends (application level UV-screen): ***a****: (◊), 0.0%; (acetyl content, 6.0%); (○), 1.5%; (Δ), 1.5% (acetyl content, 6.0%).* ***b****: (◊), 0.0%; (acetyl content, 6.0%); (○), 1.4%; (Δ), 1.2% (acetyl content, 6.0%).* ***c****: (◊), 0.0%; (acetyl content, 6.0%); (○), 2.0%; (Δ), 1.7% (acetyl content, 6.0%).*

Fig. 8. The change in TAPPI brightness after sequential irradiation (UV-fluorescent lamps and UV/VIS-fluorescent lamps) of hydrogen-peroxide-bleached aspen CTMP. Filled symbols indicate that the handsheets have been irradiated with only one of the light sources. Abbreviations as in Fig. 1. Legends (acetyl content): (□), untreated; (◊), 4.1%; (○), 10.3%.

Table 1. Change in optical properties on acetylation of different high-yield pulps. Acetylation times (min) are given within parentheses.

Pulp		Acetyl content, % by mass	TAPPI brightness, %	L*	a*	b*	PC_1-number[a]
TMP (spruce), dithionite-bleached							
Control		1.4	65.7	92.1	-0.4	13.6	0.00
Acetylated	(5)[b]	6.2	66.5	92.4	-0.5	13.2	-0.52
	(15)[b]	10.6	67.5	92.8	-0.6	13.0	-1.13
TMP (spruce), H_2O_2-bleached							
Control		0.2	75.0	95.0	-1.7	10.7	0.00
Acetylated	(5)[b]	3.5	73.7	94.9	-1.8	11.6	0.53
	(15)[b]	6.7	72.7	94.9	-1.9	12.4	0.93
CTMP (spruce), H_2O_2-bleached							
Control		0.5	78.2	95.4	-1.9	8.8	0.00
Acetylated	(5)[b]	4.6	76.3	95.2	-2.0	10.0	0.64
	(15)[b]	9.4	75.6	95.1	-2.1	10.4	0.90
CTMP (aspen), H_2O_2-bleached							
Control		0.6	84.3	95.8	-1.0	4.3	0.00
Acetylated	(5)[b]	4.1	80.9	95.3	-1.4	6.4	0.87
	(10)[b]	6.0	78.5	94.9	-1.3	7.6	1.56
	(10)[c]	9.7	74.3	93.7	-1.1	8.8	3.06
	(25)[b]	10.3	73.7	93.7	-1.1	9.3	3.31

[a]The post-color (PC_1) number at 457 nm (due to acetylation) was calculated according to Giertz (1945), Eqs. [1] and [2].

[b]Acetylation temperature, 100 °C.

[c]Acetylation temperature, 110 °C.

Table 2. Change in optical properties on light-induced aging of untreated and acetylated high-yield pulps. Acetylation times (min) are given within parentheses.

Pulp	Acetyl content, % by mass	TAPPI brightness, %	UV-fluorescent lamps Irradiation time: 4 h			UV/VIS-fluorescent lamps Irradiation time: 216 h			Xenon lamp Irradiation time: 40 h		
			TAPPI brightness, %	PC_2-number[a]	Δk[b]	TAPPI brightness, %	PC_2-number[a]	Δk[b]	Brightness[c], %	PC_2-number[a]	Δk[b]
TMP (spruce), dithionite-bleached											
Control	1.4	65.7	45.6	23.4	10.3	45.6	23.3	10.3	44.9	24.6	10.9
Acetylated (5)[d]	6.2	66.5	50.9	15.3		60.7	4.3		54.1	11.3	
(15)[d]	10.6	67.5	56.2	9.3		68.3	-0.5		60.1	5.5	
TMP (spruce), H_2O_2-bleached											
Control	0.2	75.0	49.7	21.3	11.2	47.3	25.2	13.3	48.4	23.5	12.4
Acetylated (5)[d]	3.5	73.7	53.9	15.1		64.8	4.9		56.2	12.6	
(15)[d]	6.7	72.7	58.5	9.6		73.9	-0.5		64.3	4.9	
CTMP (spruce), H_2O_2-bleached											
Control	0.5	78.2	49.6	22.5	10.9	48.2	24.8	12.0	48.4	24.4	11.8
Acetylated (5)[d]	4.6	76.3	53.0	17.2		63.9	6.5		55.5	14.4	
(15)[d]	9.4	75.6	59.0	10.3		73.5	0.8		61.5	8.4	
CTMP (aspen), H_2O_2-bleached											
Control	0.6	84.3	55.6	16.2	6.2	66.5	7.0	2.7	58.2	13.4	5.1
Acetylated (5)[d]	4.1	81.0	59.0	12.0		77.0	1.3		64.0	8.2	
(10)[d]	6.0	78.6	61.2	9.3		80.0	-0.4		67.7	5.1	
(10)[e]	9.7	74.6	63.8	6.1		81.5	-2.1		70.7	2.3	
(25)[d]	10.3	73.7	64.5	5.0		82.1	-2.5		70.8	1.9	

[a]The post-color (PC_2) number at 457 nm (due to irradiation) was calculated according to Giertz (1945), Eqs. [1] and [2].

[b]The change in light absorption (Δk) was calculated from the PC_2-value with the assumption of constant light scattering according to Johnson (1989), Eq. [3].

[c]Brightness measured with an Elrepho 2000 spectrophotometer. This instrument uses a diffuse light source and measures the reflected light at a 0° viewing angle, i.e., the "Elrepho" brightness cannot directly be translated to TAPPI brightness that is determined with an instrument employing a directional light source (incident angle of 45°) and measures the reflected light at a 0° viewing angle. The difference in measured brightness was, however, small between the two instruments (less than 1 brightness unit).

[d]Acetylation temperature, 100° C.

[e]Acetylation temperature, 110° C.

Table 3. Change in optical properties on light-induced aging of untreated, acetylated and/or 2-hydroxy-4-methoxybenzophenone (HMB) impregnated aspen CTMP. Footnotes as in Table 2.

Pulp	Acetyl content, % by mass	HMB wt%	TAPPI brightness, %	UV-fluorescent lamps Irradiation time: 2 h			UV/VIS-fluorescent lamps Irradiation time: 408 h			Xenon lamp Irradiation time: 40 h		
				TAPPI brightness, %	PC_2-number[a]	Δk[b]	TAPPI brightness, %	PC_2-number[a]	Δk[b]	Brightness[c], %	PC_2-number[a]	Δk[b]
Aspen CTMP												
Control	0.6	0.0	84.3	60.9	11.1	4.3	59.4	12.5	4.8	58.2	13.2	5.1
Acetylated	6.0	0.0	78.6	65.0	6.5		76.4	0.7		67.7	5.1	
HMB	0.6	1.5	79.7	69.4	4.2							
HMB	0.6	1.4	80.7				60.0	11.0				
HMB	0.6	2.0	80.1							70.1	3.9	
Acetylated/HMB	6.0	1.5	78.1	68.7	4.1							
Acetylatcd/HMB	6.0	1.2	77.4				78.0	-0.2				
Acetylated/HMB	6.0	1.7	78.8							76.9	0.6	

Figure 1

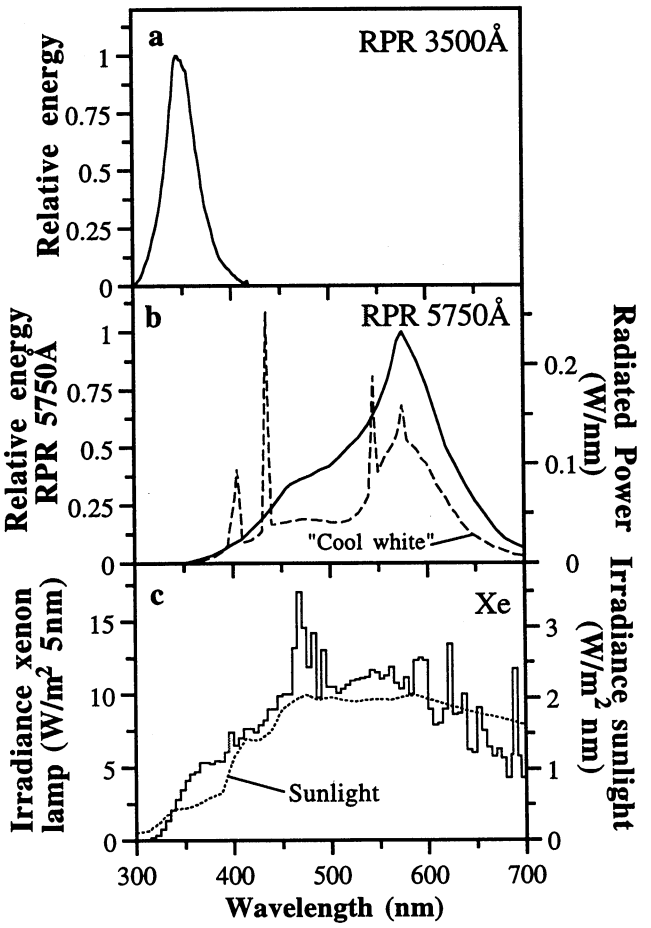

a
RPR 3500Å
Relative energy
b
RPR 5750Å
Relative energy RPR 5750Å
Radiated Power (W/nm)
"Cool white"
c
Xe
Irradiance xenon lamp (W/m² 5nm)
Irradiance sunlight (W/m² nm)
Sunlight
Wavelength (nm)

Figure 2

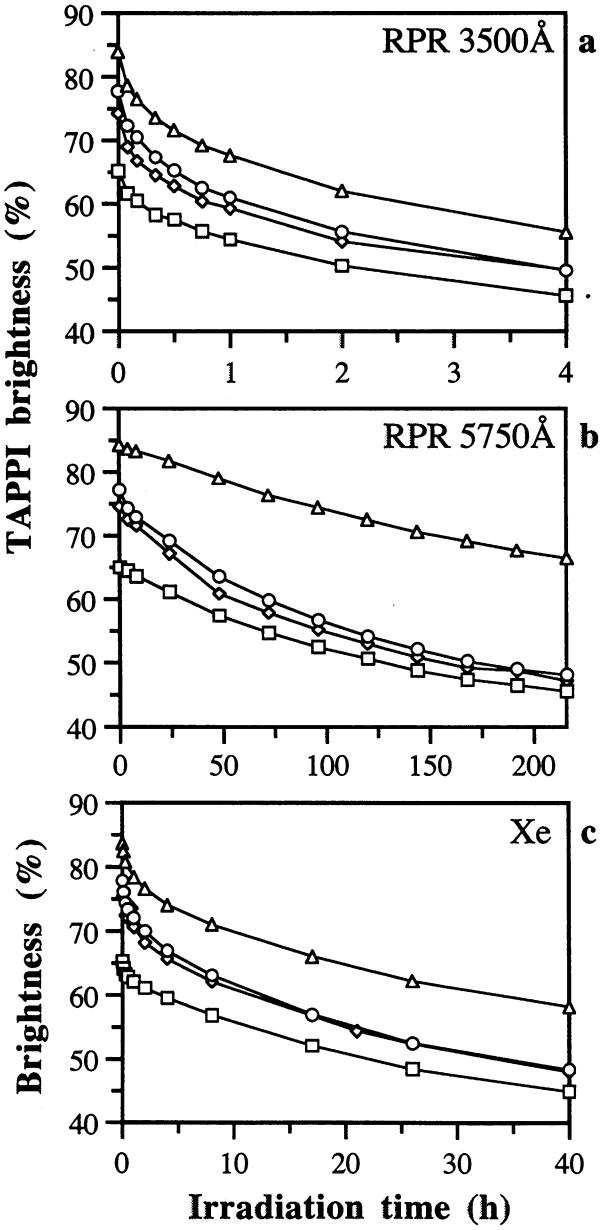

RPR 3500Å
a
RPR 5750Å
b
Xe
c
TAPPI brightness (%)
Brightness (%)
Irradiation time (h)
90
80
70
60
50
40
0
1
2
3
4
50
100
150
200
10
20
30
40

Figure 3

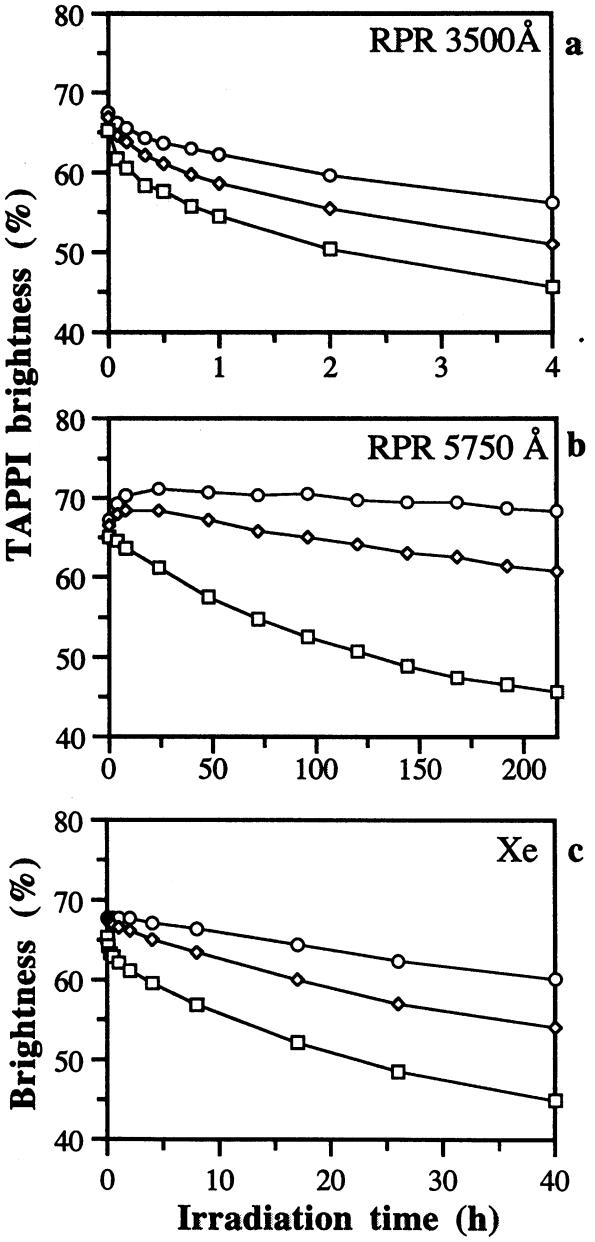

RPR 3500Å
a
RPR 5750 Å
b
Xe
c
TAPPI brightness (%)
Brightness (%)
Irradiation time (h)
80
70
60
50
40
0
1
2
3
4
50
100
150
200
10
20
30

Figure 4

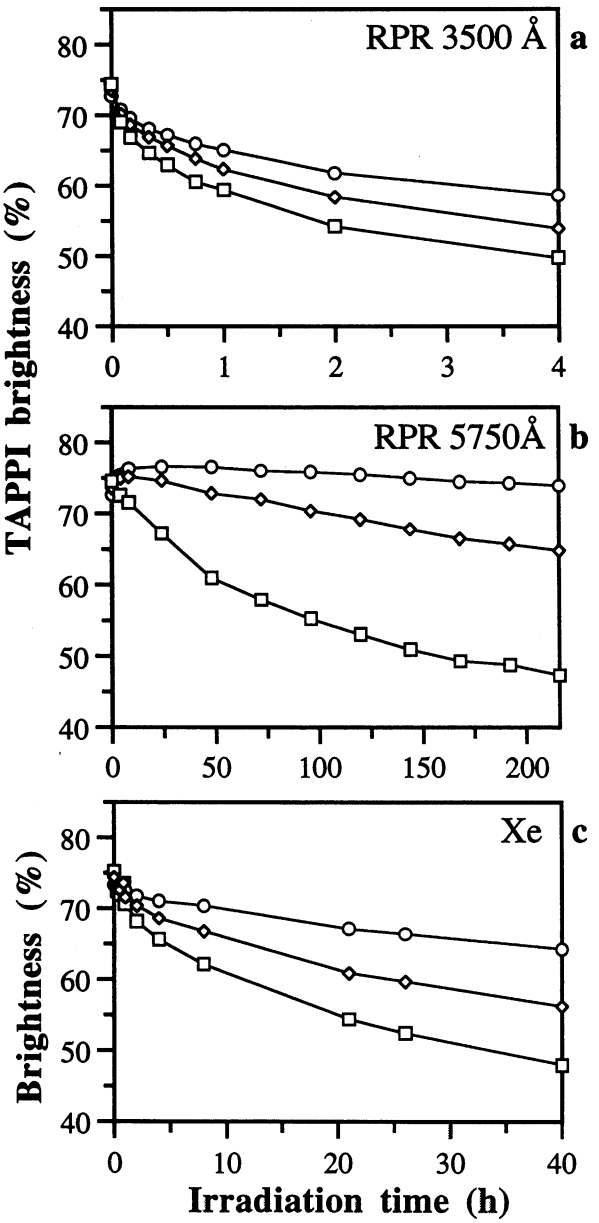

RPR 3500 Å
a
RPR 5750Å
b
Xe
c
TAPPI brightness (%)
Brightness (%)
Irradiation time (h)
80
70
60
50
40
0
1
2
3
4
50
100
150
200
10
20
30

Figure 5

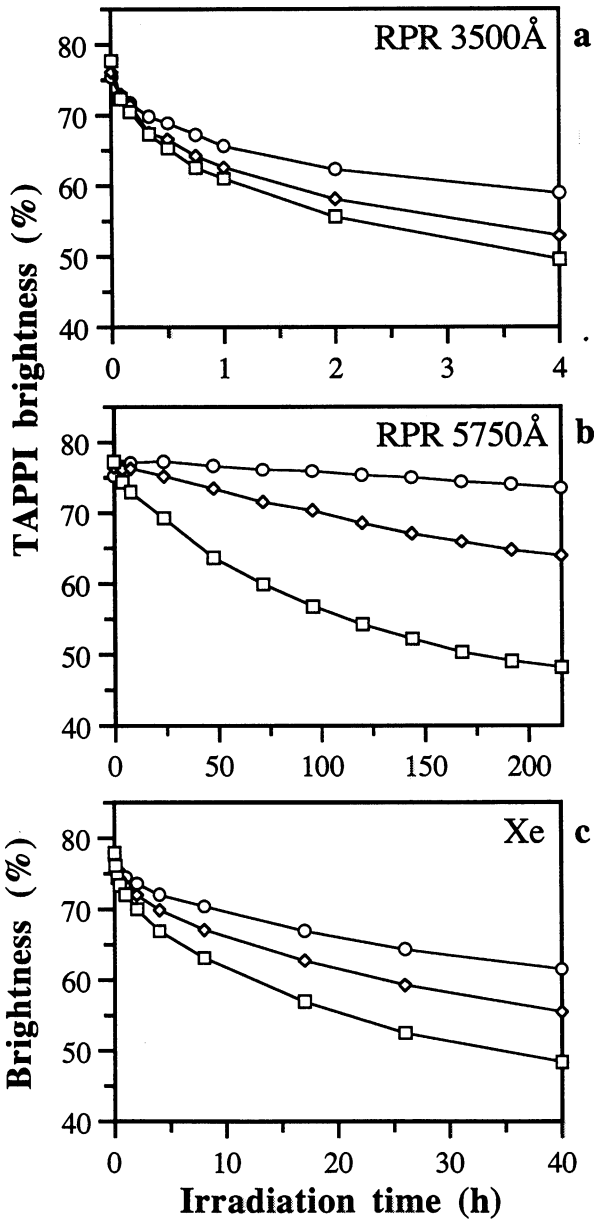

RPR 3500Å
a
RPR 5750Å
b
Xe
c
TAPPI brightness (%)
Brightness (%)
Irradiation time (h)
80
70
60
50
40
0
1
2
3
4
50
100
150
200
10
20
30

Figure 6

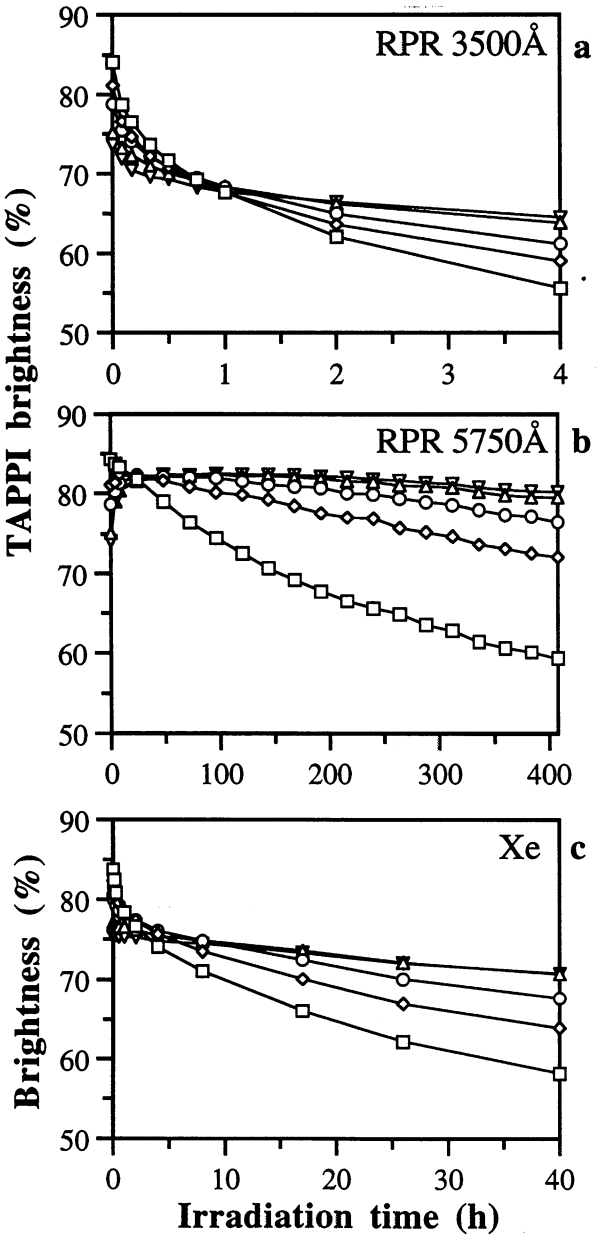

RPR 3500Å
a
RPR 5750Å
b
Xe
c
TAPPI brightness (%)
Brightness (%)
Irradiation time (h)
90
80
70
60
50
0
1
2
3
4
100
200
300
400
10
20
30
40

Figure 7

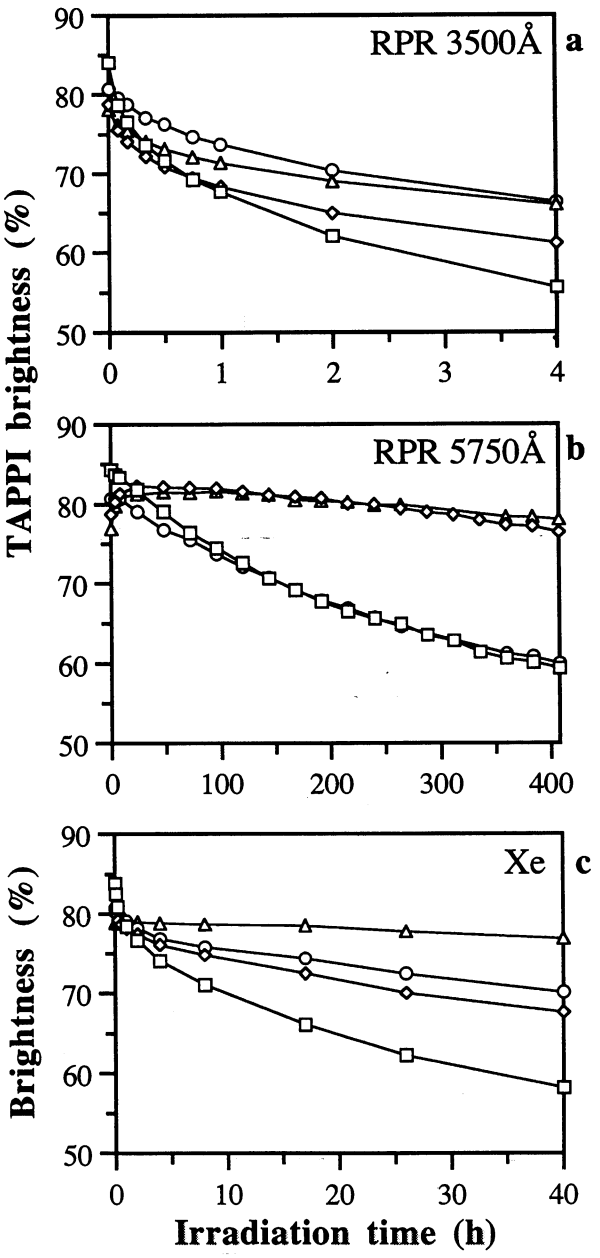
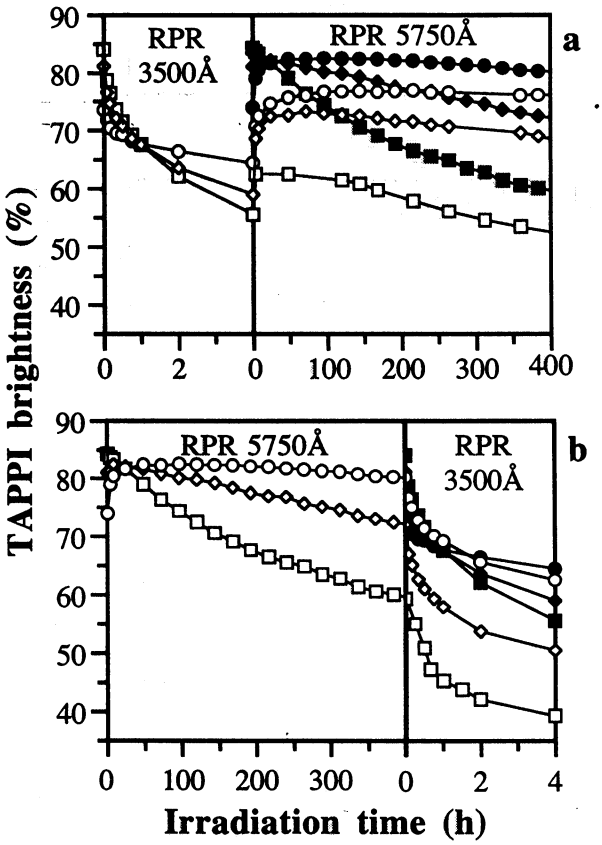

RPR 3500Å
a
RPR 5750Å
b
Xe
c
TAPPI brightness (%)
Brightness (%)
Irradiation time (h)
90
80
70
60
50
0
1
2
3
4
100
200
300
400
10
20
30
40

Figure 8


RPR
3500Å
RPR 5750Å
a
RPR 5750Å
RPR
3500Å
b
TAPPI brightness (%)
Irradiation time (h)
90
80
70
60
50
40
0
2
100
200
300
400
4